

PATENT SPECIFICATION

(11) 1 218 456

NO DRAWINGS

1218456

- (21) Application No. 42478/68 (22) Filed 6 Sept. 1968
 (23) Complete Specification filed 20 May 1969
 (45) Complete Specification published 6 Jan. 1971
 (51) International Classification C 07 c 7/18, 11/16
 (52) Index at acceptance C5E 5G 7A3 7AY 9A
 (72) Inventor HUBERT CHARLES BAILEY



(54) PROCESS FOR THE STABILISATION OF BUTADIENE

(71) We, BP CHEMICALS (U.K.) LIMITED, of Britannic House, Moor Lane, London, E.C.2., England, a British company, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the stabilisation of butadiene.

Butadiene is formed as a valuable by-product in the steam cracking of naphtha to produce ethylene as the main product. The product from the cracking operation is fractionated and butadiene appears in the C₄ fraction together with butene-1, butene-2, isobutene, small amounts of butane and isobutane and traces of acetylenes.

One process for the recovery of butadiene involves the extractive distillation of such a fraction with acetonitrile. Butadiene passes into the acetonitrile extract and is recovered from the latter by stripping.

Unfortunately, butadiene tends to polymerise under extractive distillation conditions. Polymer deposits form on the extractive distillation column and on subsequent items of equipment such as pumps. These deposits interfere with the efficient operation of the plant and eventually build up to such an extent that the plant must be shut down for cleaning. Shut downs can occur at frequent intervals and the resulting loss of production can be considerable.

It is believed that free radicals derived from butadiene can function in two ways. In the presence of oxygen, peroxy radicals are formed which eventually form butadiene poly peroxides. In the absence of oxygen, oligomers of butadiene are produced. Under plant conditions, it is very difficult to exclude oxygen and explosions have occurred as a result of poly peroxide formation. Furthermore, poly peroxides act as polymerisation initiators.

Two approaches have been made in attempts

to solve the problem of polymer formation and deposition.

The addition of a controlled quantity of molecular oxygen to butadiene could, in principle, be used to stabilise the butadiene against polymerisation. An anti-oxidant may be added to the butadiene to give more satisfactory inhibition than is obtained by molecular oxygen alone. However, if oxygen has been used to inhibit polymerisation of butadiene and the oxygen supply is cut off, polymerisation is more likely to take place than if no oxygen whatsoever has been used. This is a great disadvantage of the use of molecular oxygen as a stabilizer. When oxygen is present, anti-oxidants such as tert. butyl catechol have been employed as peroxy traps. These, however, are unsuited to the stabilization of butadiene in distillation systems. Because of their low volatility relative to butadiene they are unlikely to reach all the surfaces in a distillation column on which butadiene might condense. At any place in the column where oxygen and butadiene are present in the absence of anti-oxidant, poly peroxide will build up and eventually initiate polymerisation. Furthermore, a dangerous situation arises if an anti-oxidant is used to stabilize butadiene in a closed system and the oxygen in that system is eventually totally converted to oxidation products. At this point, the anti-oxidant will be unable to prevent peroxide-initiated polymerisation, since the primary inhibitor, that is oxygen, has been exhausted.

When oxygen is absent, nitric oxide has been employed as a hydrocarbon radical trap to stabilize butadiene. While this is a satisfactory method if oxygen can be rigorously excluded, it is unsatisfactory when oxygen leaks into the system. If this occurs, nitric oxide is rapidly converted to nitrogen dioxide which is a less effective stabilizer and adducts of butadiene with nitric oxide will form. Nitrogen dioxide, produced from nitric oxide, adds, together with nitric oxide, to the double bonds

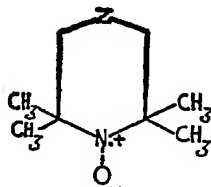
of butadiene. Nitro, nitrite and nitroso groups are formed, probably mainly in the 1,4 positions of butadiene.

Thus neither method is suitable for use on industrial plant where there is neither an excess of oxygen available nor an absence of oxygen.

We have now discovered that certain nitroxides are suitable stabilizers for butadiene under extractive distillation conditions. They inhibit polymerisation at elevated temperature and act in the absence of oxygen although they can tolerate the presence of oxygen and do not give undesirable compounds when the latter is present.

It will be appreciated that the ability of the nitroxide to function both in the presence and absence of oxygen is a marked improvement over the prior art in which a choice had to be made between an oxygen-free and an oxygen-containing system, and in which any change from one system to the other would lead to highly undesirable results.

British Patent Specification 983,134 discloses a cyclic nitroxide of formula



In which Z is

>CH_2 , >CHCH_3 , >C=O , >CHBr ,
 >CHCl , >CHI , >CHF , >CHOH ,
 >CHCN , >C(OH)CN , >CHCOOH ,
 >CHCOOCH_3 , $\text{>CHCOOC}_2\text{H}_5$,
 $\text{>C(OH)COOC}_2\text{H}_5$, or $\text{>C(OH)CHOHC}_2\text{H}_5$.

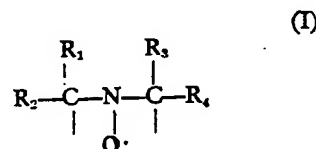
and, in particular, 2,2,6,6-tetra methyl piperidine nitroxide.

It further discloses that these compounds are stable free radicals and as such are useful as polymerisation-inhibitors, anti-knock agents in fuels and anti-oxidants for rubber. Additionally, such N,N-disubstituted nitroxides are useful as traps for reactive free radicals and as paramagnetic standards for electron spin resonance spectrometry.

However, stable radicals can in principle both initiate and terminate radical polymerisation reactions. With increasing temperature, their initiating action will become relatively more pronounced, because termination is a radical/radical reaction, requiring 0 or a low energy of activation, while the addition of a radical to a monomer usually requires energy of activation exceeding 5 kcal./mol.

Thus, although 983,134 discloses that nitroxide radicals are polymerisation inhibitors, it is not obvious that they would be particularly effective at relatively high temperatures (60°C. and above).

According to the present invention there is provided a process for the stabilisation of butadiene at elevated temperature which process comprises adding to the butadiene a nitroxide having the essential skeletal structure:



wherein R_1 , R_2 , R_3 and R_4 are alkyl groups and no hydrogen is bound to the remaining valencies on the carbon atoms bound to nitrogen.

The alkyl groups R_1 to R_4 may be the same or different, and preferably contain 1 to 15 carbon atoms. It is particularly preferred to use nitroxides having the essential skeletal structure (I) in which R_1 to R_4 are methyl, ethyl or propyl groups.

The remaining valencies of the carbon atoms in the essential skeletal structure which are not satisfied by R_1 — R_4 or nitrogen may be satisfied by any atom or group except hydrogen which can bond covalently to carbon although some groups may reduce the stabilizing power of the nitroxide structure (I) and are undesirable. Examples of suitable

atoms or groups are halogen, cyanide $\text{—C}\begin{smallmatrix} \text{O} \\ \text{OR} \end{smallmatrix}$

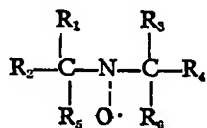
when R is alkyl or aryl, $\text{—C}\begin{smallmatrix} \text{O} \\ \text{NH}_2 \end{smallmatrix}$, —SPh ,

—S—COCH_3 , —OCOCH_3 , $\text{—OCOC}_2\text{H}_5$, alkenyl where the double bond is not in conjugation with the group



and alkyl. The two remaining valencies which are not satisfied by R_1 to R_4 or nitrogen may also form part of a ring. Examples of suitable compounds having the essential skeletal structure (I) and in which the remaining valencies of (I) form part of the ring are pyrrolidine-1-oxyls and piperidine-1-oxyls. A particular example of a suitable compound in which the remaining valencies of the essential skeletal structure (I) form part of a ring is 2,2,6,6-

tetramethyl - 4 - hydroxy - piperidine - 1 - oxyl. Where the remaining valencies of (I) are satisfied by alkyl groups R_5 , R_6 to give a compound of formula



(II)

the groups R_5 and R_6 preferably contain 1 to 15 carbon atoms. Examples of suitable groups R_5 and R_6 are methyl, ethyl and propyl groups. A specific example of a suitable compound having the essential structure (I) is di-tert-butyl nitroxide.

Although as we have indicated above it is possible to stabilize butadiene in the presence of oxygen, for the very best results it is preferred to exclude oxygen and oxygen yielding materials. In the presence of oxygen peroxy compounds of butadiene tend to be formed, which on decomposition lead to the consumption of nitroxide. However, the compositions of the present invention will still be stabilized against polymerization in oxygen concentrations in the butadiene of up to those present in a monomer in equilibrium with air at atmospheric pressure. This is extremely useful as there is therefore no need to purge the buta-

diene with inert gas to remove dissolved oxygen. This is in marked contrast to monomers stabilized with some other inhibitors effective in the absence of oxygen. Thus nitric oxide may be used to inhibit the polymerisation of monomers in the absence of oxygen but where oxygen is present the inhibiting action of nitric oxide is lost.

Suitably the nitroxide is employed in a concentration in the range 10 to 1000 parts per million parts of butadiene.

The nitroxides are most suitable for use at distillation temperatures in the range 60 to 130°C.

The nitroxides may be prepared by the method disclosed by O. L. Lebedev and S. N. Kazamovski, Tr. po. Khim. i Khim. Tekhnol. 2, 649-656 (1959).

The invention is illustrated by the following examples.

EXAMPLE 1

3% by weight solutions of butadiene in acetonitrile, containing di-tert. butyl peroxide as initiator and either 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl or Cupferron (ammonium - N - nitrosophenyl - hydroxylamine) as inhibitor, were sealed in a dilatometer under vacuum. The induction periods before the onset of rapid polymerisation were then measured at 130°C.

Concentration of di-tert-butylperoxide $10^3 \times \text{mole/litre}$	Inhibitor			Induction period, minutes
	Compound	Concentration $10^3 \times \text{mole/litre}$	Concentration p.p.m. by wt.	
5.3	None	0	0	0
5.1	Cupferron	4.9	960	40
5.3	2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl	4.9	1090	133

The effectiveness of the nitroxide and its superiority over Cupferron is evident.

EXAMPLE 2

3% by weight solutions of butadiene in acetonitrile containing di- α -cumylperoxide as initiator, and either 2,2,6,6-tetramethyl-4-

hydroxy - piperidine - 1 - oxyl or the stable radical DPPH (1,1'-diphenyl-2-picrylhydrazil) as inhibitor, were sealed in tubes under vacuum and heated at 100°C. The induction periods before the visible formation of polymer were then observed.

Concentration of di-cumyl-peroxide $10^3 \times$ mole/litre	Inhibitor			Induction period, minutes
	Compound	Concentration $10^3 \times$ mole/litre	Concentration p.p.m. by wt.	
3.6	None	0	0	20
3.7	DPPH	6.7	342	220
3.5	2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl	6.6	146	420

The effectiveness of the nitroxide and its superiority over DPPH is evident.

EXAMPLE 3

5 10% by weight solutions of butadiene in

acetonitrile, containing azobis(isobutyronitrile) as initiator and various inhibitors, were sealed in a dilatometer in vacuum and heated at 60°C . The induction periods before the onset of rapid polymerisation were measured.

10

Concentration of azobis(isobutyronitrile) $10^2 \times$ mole/litre	Inhibitor			Induction period minutes
	Compound	Concentration $10^3 \times$ mole/litre	Concentration p.p.m. by wt.	
4.0	None	0	0	8
4.0	t-Butylcatechol	4.5	986	11
4.0	2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl	4.4	995	130
3.9	2,2,6,6-tetramethyl-piperidine-1-oxyl	4.9	996	168

The two nitroxides were of similar reactivity and greatly superior to tert.butylcatechol.

EXAMPLE 4

15 To each of two tubes a 4 ml. portion of acetonitrile, saturated at ambient temperature with air, was added. The tubes were frozen in liquid oxygen and evacuated. In each enough butadiene was distilled to give a 3% by weight solution in acetonitrile; the tubes were then sealed under vacuum. One tube contained in addition the inhibitor 2,2,6,6-tetra-

methypyrrolidine-1-oxyl. Both tubes contained a small amount of oxygen from the air with which the acetonitrile had been saturated.

A third tube containing 3% by weight of butadiene in acetonitrile and the nitroxide inhibitor was also sealed under vacuum. In this instance the acetonitrile was thoroughly degassed under vacuum before adding the butadiene, so that no oxygen was present in this tube.

All the tubes were then heated at 130°C . and the times taken for the visible formation of a haze of polybutadiene were observed.

25

30

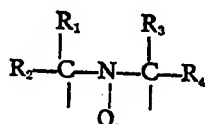
35

Inhibitor		Oxygen	Time to cloudiness
Compound	p.p.m. by wt.		
None	0	present	10 minutes
2,2,6,6-tetramethylpyrrolidine-1-oxyl	53	present	23 days
2,2,6,6-tetramethylpyrrolidine-1-oxyl	53	absent	22 days

5 The powerful stabilising action of the nitroxide is readily apparent; in addition the nitroxide was as effective in the presence of a trace of oxygen as in the absence of oxygen.

WHAT WE CLAIM IS:—

1. A process for the stabilisation of butadiene at elevated temperature which process comprises adding to the butadiene a nitroxide having the essential skeletal structure:



15 wherein R_1 , R_2 , R_3 and R_4 are alkyl groups and no hydrogen is bound to the remaining valencies on the carbon atoms bound to nitrogen.

2. A process according to claim 1 wherein the alkyl groups contain 1—15 carbon atoms.

3. A process according to claim 2 wherein the alkyl groups are methyl, ethyl, or propyl groups.

4. A process according to claim 3 wherein the nitroxide is a piperidine-1-oxyl.

5. A process according to claim 4 wherein the piperidine-1-oxyl is 2,2,6,6-tetramethyl-4-hydroxy piperidine-1-oxyl.

6. A process according to any of the preceding claims wherein the nitroxide is employed in a concentration in the range 10 to 1000 parts per million parts of butadiene.

7. A process according to any of the preceding claims wherein the butadiene is stabilised at a temperature in the range 60° to 130°C.

8. A process according to claim 1 as hereinbefore described with reference to the examples.

9. Butadiene whenever stabilised by a process according to any of the preceding claims.

JOHN HARRY,

Agent for the Applicants,